

# Investigation on the Long-Term Behavior of Polyethylene and Poly(vinyl chloride) under Static Load

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## Synopsis

The long-term behavior of high density polyethylene (HDPE) and poly(vinyl chloride) (PVC) under static mechanical load is investigated. The long-term behavior is determined as a function of stress and temperature. The applicability of the equation proposed by the authors which describes the dependence between the time-dependent failure, stress, and temperature of the two polymers is examined. The equation, derived on theoretical considerations, represents a modification of the Arrhenius equation for the chemical reaction rate. It is found that there is a complete agreement between the experimentally determined long-term behavior of PVC and HDPE and that calculated by the equation over the whole examined range of temperatures and stresses, with the exception of narrow intervals for HDPE where an intensive plastic deformation is developed.

## INTRODUCTION

Currently, the theory of the polymer fracture is based on the kinetic concept of the nature of the process.<sup>1,2</sup> According to this concept, decomposition of chemical bonds is accomplished by thermofluctuation under the action of mechanical stress. That is why all hypotheses, which have been proposed for explanation of the kinetics of polymer fracture, are based on the well-known Arrhenius equation for the rate of chemical processes:

$$V = K \cdot \exp(-E/RT) \quad (1)$$

where  $V$  = rate of the chemical reaction,  $K$  = rate constant,  $E$  = activation energy of the process,  $R$  = universal gas constant, and  $T$  = absolute temperature.

The long-term stability behavior is the reciprocal to the fracture rate—the time from the begin of stress application up to polymer fracture. It is known from theoretical considerations that if the activation energy is reduced by the stress, then its influence will be accounted for in the numerator of the exponent coefficient in the Arrhenius equation by a second term. Such equations are proposed by Tobolsky and Eyring,<sup>3</sup> Bueche,<sup>4</sup> Jurkov and Abasov,<sup>5</sup> Bartenev,<sup>6</sup> and Gul.<sup>7</sup> The equations based on the assumption that the mechanical stress has an effect on the activation energy only lead to the conclusion that the logarithm of the polymer long-term behavior should be the linear function of the applied mechanical stress. Furthermore, it is supposed that the linear dependences at different temperatures coincide at

one point, corresponding to the value of the vibration frequency of the polymer particles.<sup>5</sup> The experimental data from highly oriented polymers like fibers confirm these assumptions. The examination of the long-term behavior of isotropic and quasiisotropic samples over a wide range of stresses and temperatures, however, shows that the dependence between the long-term logarithm and the stress is not linear but a considerably more complicated function.<sup>8-10</sup>

If the vibration frequency of the polymer kinetic units is changed under the mechanical action of stress—an action which is analogous to that of temperature—then the stress influence must be expressed in the exponent coefficient denominator of the Arrhenius equation. Considering the analogy between temperature and stress, the following equation for the polymer long-term behavior description was proposed<sup>1</sup>:

$$\tau = \tau_0 \cdot \exp\left(\frac{U}{RT + \alpha \cdot \sigma^n}\right) \quad (2)$$

where  $\tau$  is the long-term behavior,  $\tau_0$  = preexponential factor, which has the value of the polymer lowest limiting long-term behavior,  $U$  = activation energy of the break process,  $R$  = universal gas constant,  $T$  = absolute temperature,  $\delta$  = the applied mechanical stress, and  $\alpha$  and  $n$  = constants.

The purpose of the present work is to examine the applicability of this equation for description of the actual long-term behavior of some semicrystalline and amorphous polymers subjected to the action of the static load over a wide time-temperature range.

## OBJECTS AND INVESTIGATION METHODS

We investigated the long-term stability [ $\tau$ , (s)] of high density polyethylene (HDPE) with melt index 2.48 g/10 min as a typical representative of a crystalline polymer, and of poly(vinyl chloride) (PVC) with a  $K$  value of 68.6 as a typical representative of an amorphous polymer. Samples for tensile strength tests are prepared by compression moulding and stamping. The time-dependent failure is examined at conditions of uniaxial tension kept constant over time. Each point on the experimental long-term behavior curve is obtained by a statistic treatment of the results from about 40 test samples.

The deformation at break [ $\epsilon$  (%)] is estimated as a change of the sample working section length immediately before fracture, divided by the initial length.

## RESULTS AND DISCUSSION

### Experimental Data from the Investigation of HDPE and PVD Long-Term Behavior

Figure 1(a) shows the results of the investigations of HDPE long-term behavior at temperatures 0, 20, 50, and 80°C and in the time interval from less than seconds up to several years (up to 12 years for the experiments at 20°C and up to 3 years at the remaining temperatures). The results obtained confirm our investigations and those of other authors<sup>8-10</sup> in that the depen-

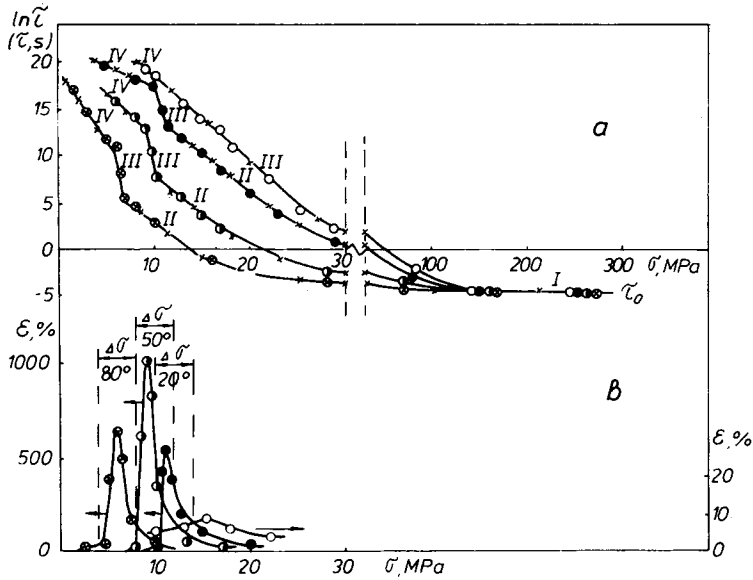


Fig. 1. Dependence of the long-term behavior (a) and the deformation at fracture (b) of HDPE on the stress at 0 (○), 20 (●), 50 (⊙), and 80°C (⊗) (experimental results): (×) = calculated values.

dence  $\ln \tau(\sigma)$  has a complicated nonlinear course and includes several sections which specify the different fracture mechanisms as a function of the applied stress. Our experiments showed that the lowest, which we call "limiting long-term behavior,"  $\tau_0$ , at higher loadings remains constant, independently of stress and temperature. That fact could be explained with the realization of fracture by an athermal mechanism. In sections II and III the character of the break process is determined by the ratio of crackformation rates by deformation and thermofluctuation process. Under the stress action in section II a crack formation process takes place at a high rate, while in section III a deformation process with crackformation is operative. The whole working section of the sample transforms into a thin fiber, and it is that transformation of structure which leads to a sharp prolongation of the material long-term behavior. In Figure 1(b) the peaks at 20, 50, and 80°C outline the range of stresses at which necking of the material occurs. At 0°C, because of the limited mobility of the polymer molecules in HDPE, a plastic deformation does not develop and the fracture is almost fully brittle over the entire stress range. In the last section (IV) again a trend towards reaching a limiting long-term behavior is observed which is lower at higher temperatures.

In Figure 2 the results from the investigations of the long-term behavior and deformation at break of PVC at 20, 50, and 80°C are shown over the same range of long-term behavior as with HDPE. While PVC is in its glass state at 20 and 50°C, it is in a high-elastic state at 80°C, which is indicated also by the values of maximum deformation at break, shown in Figure 2(b). Also with this polymer the complicated course of the dependence  $\ln \tau(\sigma)$  is confirmed, as well as the invariance of  $\tau_0$  with temperature. The necking of PVC at 80°C is considerably less than for HDPE and does not lead to a sharp prolongation of

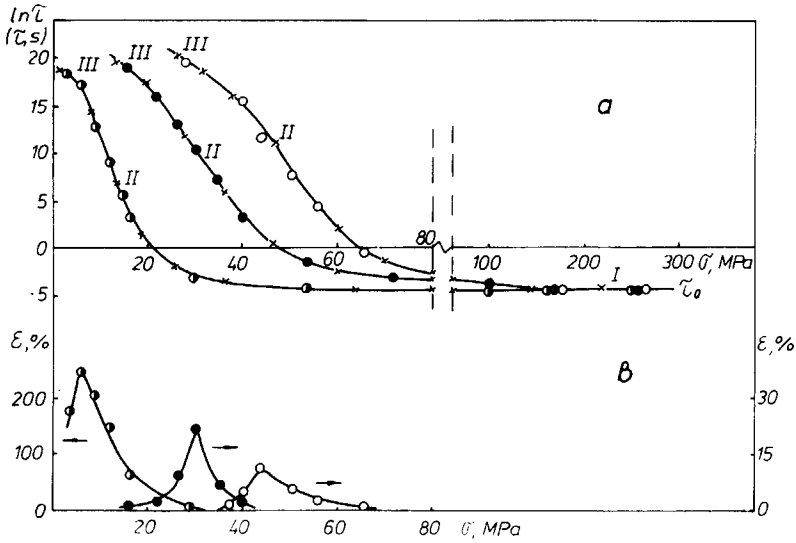


Fig. 2. Dependence of the long-term behavior (a) and the deformation at fracture (b) of PVC on the stress at 20 (○), 50 (●), and 80°C (⊙) (experimental results); (×) calculated values.

the long-term behavior. With PVC, as with HDPE, the last section III on the long-term behavior curve shows a trend towards reaching a constant level of highest long-term behavior.

### Comparability between the Experimental Results and the Proposed Analytical Model for Long-Term Behavior

As the experiments for the investigation, the long-term behavior of the two polymers are carried out over a wide time-temperature range, a reliable assessment for the validity of the proposed equation, eq. (2), could be accomplished on the basis of these investigations.

If it is assumed that the experimentally found dependence  $\ln \tau(\sigma, T)$  for HDPE and PVC can be expressed by eq. (2), then the values of  $\tau_0$ ,  $U$ ,  $\alpha$ , and  $n$  could be calculated. These values are independent of stress and, accordingly, the analytical model is in rather close agreement with the dependences which have been found experimentally. The calculated values are shown in Table I.

TABLE I

Polymer	$T$ [K (°C)]	$\ln \tau_0$	$\tau_0$ (ms)	$U$ (J/mol)	$n$	$\alpha$ (J/MPa <sup><math>n</math></sup> mol)
HDPE	273 (0)	-4.66	9.47	58,890	2.80	0.49
	293 (20)	-4.66	9.47	61,990	2.55	1.60
	323 (50)	-4.66	9.47	64,850	2.65	3.91
	353 (80)	-4.66	9.47	67,940	1.90	78.93
PVC	293 (20)	-4.70	9.09	62,570	5.50	$1.10 \times 10^{-6}$
	323 (50)	-4.70	9.09	66,830	4.20	$1.10 \times 10^{-3}$
	353 (80)	-4.70	9.09	68,350	3.20	0.80

In order to check if this mathematical model is in accordance with the experimental data, the experimental values of  $\ln \tau$  are compared to those calculated using the model, denoted in Figures 1(a) and 2(a) by  $\times$ . This comparison shows the following:

For PVC at all three temperatures and for HDPE at 0°C the calculated values of  $\ln \tau$  are within the confidence interval of the experimental values over the whole time range.

For HDPE at 20, 50, and 80°C there is a very good coincidence of the values, with the exception of those regions where the necking causes a sharp, discontinuous change of the long-term behavior. These regions are designated by  $\Delta\sigma$  in Figure 1(b). In these ranges the sharp change of the long-term behavior curve is related also to a change of the constants values for the respective temperatures.

Hence, if the experimental conditions do not allow the development of an intensive plastic deformation which leads to a discontinuous change of the sample structure, or of the material long-term behavior, respectively, then the long-term behavior of HDPE and PVC over a wide time-temperature range can be expressed by the equation

$$\tau = \tau_0 \cdot \exp \left[ \frac{U(T)}{RT + \alpha(T) \cdot \sigma^{n(T)}} \right] \quad (3)$$

where at a given temperature the constants  $U$  and  $n$  have a constant value, and  $\tau_0$  is a material constant and does not depend on temperature.

#### Interpretation of the Quantities Contained in the Equation

As the proposed equation is a modification of the Arrhenius equation for the rate of chemical reactions the interpretation traced back to its physical meaning leads to the following conclusions:

The magnitude  $\exp[U/(RT + \alpha\sigma^n)]$  is inversely proportional to the number of elementary acts for the decomposition of chemical bonds and intermolecular forces, leading to solid fracture. In this process  $\sigma$  and  $T$  act in the same direction, expressed as a change of the thermal fluctuation frequency of the constituent particles. With the rise of the temperature and of the stress, respectively, the number of fracture acts per unit time increases, which leads to an acceleration of the fracture process and to the reduction of the long-term stability. The magnitudes  $\alpha$  and  $n$  determine the stress part in the change of the thermal-fluctuation frequency. The magnitude  $\tau_0$ , according to the equation, is identified with the long-term behavior at

$$\frac{U}{RT + \alpha\sigma^n} = 0$$

i.e., at very high values of the applied stress. The values of  $\tau_0$  are probably determined by the propagation of the crack formation impulse along the sample cross section. Therefore, the larger is the cross section, the lower is the long-term stability  $\tau_0$ .<sup>12</sup>

From the kinetic point of view, the energy  $U$  of the fracture process represents the difference between the energy level of the constituent particles in bonded and free state. In the light of this interpretation  $U$  gains a more concrete meaning and assumes values, respectively, which depend on the specificity of the examined objects. In investigations of highly oriented polymers in form of fibers in Jurkov's work,  $U$  has values which are very close to the energy of the thermodestruction process in its first stage, i.e.,  $U$  is identified with the decomposition energy of so-called "weak" chemical bonds in the polymer.<sup>13</sup> However, investigations of isotropic and quasiisotropic polymers as those in the present case as well as those used in investigations of other authors<sup>14</sup> show that  $U$  has considerably lower values than the thermodestruction energy which is 105 kJ/mol [23 kcal/mol]<sup>13,15</sup> for HDPE and 134 kJ/mol for PVC.<sup>15</sup> Obviously, while in fibers the fracture is determined only by the decomposition of chemical bonds in the macromolecules, oriented entirely in the applied stress direction, in isotropic and quasiisotropic polymers, besides that process, the fracture is determined also by the overcoming the forces between macromolecules which have a considerably lower energy barrier. Hence, for the objects examined in the present work  $U$  is a complex magnitude which includes the energy barriers of chemical and physical processes the value of which is determined by the contribution of these processes to the overall fracture process. This conclusion is in good agreement with the results of other authors.<sup>14</sup> With the rise of temperature the mobility of polymer macromolecules becomes higher, and they are more and more oriented in the direction of the applied stress. This is a precondition for an enhancement of the contribution of mechanochemical destruction to the overall fracture process. That could explain the weak increase of  $U$  at HDPE and PVC with the rise of temperature.

## CONCLUSIONS

1. The long-term behavior of HDPE and PVC, as representatives of crystalline and amorphous polymers, is investigated over a wide time-temperature range and at conditions of static loads. The results confirm the complicated course of the dependence  $\ln \tau(\sigma)$ .
2. On the basis of the experiments carried out, the applicability of the equation proposed by the authors is examined which describes the actual long-term behavior of the investigated polymers. It is found that there is a complete agreement between the experimental long-term behavior and that calculated according to the equation over the whole time-temperature range for PVC and also for HDPE with the exception of a narrow stress range at the temperatures at which an intensive plastic deformation develops, leading to necking which causes a discontinuous change of the long-term behavior.
3. The results show that the equation which has been proposed on theoretical considerations is appropriate for a mathematical simulation of the long-term behavior dependence on stress and temperature for the polymers investigated, and probably could be applicable also to other crystalline and amorphous polymers for which the function  $\ln \tau(\sigma, T)$  behaves in an analogous fashion to that observed with the polymers investigated here.

### References

1. G. Kaush, *Razrushenie Polymerov*, Mir, Moscow, 1981, p. 76.
2. A. G. Adamovich and Iu. S. Urjuntzev, *Mech. Kompos. Mater.*, 694 (1979).
3. A. Tobolsky and H. Eyring, *J. Chem. Phys.*, **11**, 125 (1943).
4. F. Bueche, *J. Appl. Phys.*, **28**, 784 (1957); **29**, 1231 (1958).
5. S. N. Jurkow and S. A. Abasov, *Visokomol. Soedin.* **3**, 441 (1961).
6. G. M. Bartenev, *Mech. Polym.*, 700 (1966).
7. V. E. Gul, *Mech. Polym.*, 474 (1968).
8. S. N. Ermolov and Iu. N. Potapov, *Mech. Polym.*, 746 (1976).
9. A. Ia. Goldman and V. V. Sterbak, *Plast. Massy*, 69 (1968).
10. M. A. Natov and S. V. Vassileva, *Angew. Makromol. Chem.*, **20**, 181 (1971).
11. M. A. Natov and S. V. Vassileva, *Plaste Kautschuk*, **29**, 424 (1982).
12. M. A. Natov, S. V. Vassileva, and M. S. Charalampiev, *Mech. Polym.*, 737 (1977).
13. A. V. Amelin, O. F. Pozdniakov, V. R. Regel, and T. P. Sanfirova, *Phys. Tviordogo Tela*, **12**, 2528 (1970).
14. G. L. Slonimskii, A. A. Askadskii, and V. V. Kazantzeva, *Mech. Polym.*, 775 (1977).
15. S. B. Ratner, *Plast. Massy*, 31 (1977); 47 (1980).

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